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(54) Abstract Title

Bleaching composition

(57) A bleaching composition is provided comprising

- a) a bleach-effective amount of an oxidoreductase;
 - b) 0 to 10 wt% of a surfactant;
 - c) less than 20 wt% of a modifier; and
 - d) an effective dry cleaning amount of densified carbon dioxide.
- It is particularly useful for removing stains from textiles.

GB 2 372 261 A

Bleaching composition

Field of the invention

The present invention relates to the field of bleaching
5 compositions to remove stains from articles, in particular
textile articles. In addition the present invention relates
to a method of preparing a bleaching composition and method
to bleach articles.

10 Background of the invention

It is known in the art to use hydrogen peroxide or organic
peracids or their precursors to remove stains from metal,
ceramic, plastic or textile articles. Notorious are tea
stains or oily tomato stains from for example tomato

15 sauces.

More recently, cleaning with carbon dioxide has been
described. Dense phase carbon dioxide has been suggested as
an alternative to perchloroethylene for health and
environmental reasons. For example, a dry cleaning system
20 in which chilled liquid carbon dioxide is used to extract
soils from fabrics is described in US-A-4 012 194.
However, it has been recognised that additives are needed
to boost the cleaning by this medium. For example, the use
of ethoxylated tertiary acetylenic alcohol and diol

25 surfactants for boosting the cleaning performance from
condensed phase carbon dioxide are taught in US-A-5 789
505. US-A-5 431 843 discloses a perhydrolysis system for
use in condensed fluid medium for bleaching of stained
garments. This perhydrolysis system comprises two essential
30 components: hydrogen peroxide and an organic peracid
precursor. The peracid may be the product of an enzymatic
hydrolysis of a substrate and a source of peroxide. The

enzymes should be esterase, lipase or protease. However, using peracids has many drawbacks. Although a better overall stain removal with the bleaching system of US-A-5 431 843 is possible when compared to hydrogen peroxide alone, to obtain these results, the bleaching process takes place for at least 1 hour. US-A-5 676 705 describes the use of organic peracid precursor in a dry cleaning process using carbon dioxide. Herein, both the preformed peracids and the directly added organic peracid precursor should be 10 soluble in densified carbon dioxide.

Although organic peracids and/or precursor systems are generally effective they still exhibit several disadvantages. For example, these precursor systems have 15 large formulation space requirements as they also need addition of hydrogen peroxide and/or a hydrogen peroxide delivery system. Consequently, a significant proportion of the cleaning formulation must be devoted to the bleach components, leaving less room for other active ingredients 20 and complicating the development of concentrated formulations. Moreover, organic precursor systems do not bleach very efficiently in situations wherein short bleach times are desired and processing environment is acidic or pH neutral.

25

Accordingly, it is an object of the invention to provide an alternative bleaching composition and method of bleaching which shows effective stain removal but does not display one or more of these drawbacks. One particular object of 30 the invention is to provide a bleaching composition and method of bleaching which are economical and require short bleach times. Another object of the invention is to provide

a bleaching composition and a method of bleaching which are particularly suitable for removing, tea and oily tomato stains.

- 5 Surprisingly, we have now found that one or more of these objects can be achieved by the inventive bleaching composition and method of bleaching.

Definition of the invention

- 10 Accordingly, in a first aspect of the invention a bleaching composition is provided comprising
- a) a bleach-effective amount of an oxidoreductase ;
 - b) 0 to 10 wt% of a surfactant;
 - c) less than 20 wt% of a modifier; and
- 15 d) an effective dry cleaning amount of densified carbon dioxide.

- In a second aspect of the invention a bleaching method is provided comprising the step of contacting an article with
- 20 a bleaching composition according to the invention.

Preferably, the inventive composition and method is suitable to bleach articles in less than 45 min.

25 Detailed description of the invention

- The present invention is particularly advantageous for bleaching methods that require a short period of time. US-A-5 431 843 describes bleaching times of 1 hour for effective stain removal. Unexpectedly we have now found
- 30 that the present invention provides effective bleaching in 45 minutes or less. Another advantage of the present invention is the simplicity. Organic peracid precursors as

described in the prior art often need a high pH to drive the perhydrolysis process. Since carbon dioxide has a low pH, special measures have to be taken to ensure the formation of relatively unstable peracids in a separate
5 premix process. Furthermore, the low temperatures used in carbon dioxide cleaning will also slow this reaction. It is believed that the oxidoreductases are able to rapidly and effectively remove stains because these oxidoreductases do not need to be formed from a precursor such as is the case
10 with organic peroxyacid precursor and hydrogen peroxide. Consequently, another advantage of the present invention is that it is remarkably effective on a variety of stains, especially tea and oily tomato stains. Without wishing to be bound by theory it is believed that because the
15 inventive oxidoreductase s are insoluble in carbon dioxide, only minute amounts will be present in the carbon dioxide phase resulting in less dye damage. The present invention is especially suitable to bleach and clean garments but may also be employed to bleach articles
20 with hard surfaces.

For purposes of the invention, the following definitions are used:

"The bleaching composition" describes the total of the
25 densified carbon dioxide, the oxidoreductase, the modifier if present and optionally other additives.

"Additives" are compounds to enhance the cleaning effect of the bleaching composition such as surfactants, whiteners, softeners, enzymes, perfume and antistat.

30 "Liquid carbon dioxide" means carbon dioxide which has a temperature of about 30°C or less.

"Supercritical fluid carbon dioxide" means carbon dioxide which is at or above the critical temperature of 31°C and the critical pressure of 7.2 Mpa (71 atmospheres) and which cannot be condensed into a liquid phase despite the

5 addition of further pressure.

The term "densified carbon dioxide" encompasses both liquid and supercritical fluid carbon dioxide.

The bleaching composition is defined as the composition wherein the actual bleaching occurs analogous to a wash
10 liquor. In practice this bleaching composition may be prepared by adding a bleaching product to the carbon dioxide analogous to adding a detergent product to the wash liquor.

15 Oxidoreductase

To the class of oxidoreductases belong all enzymes catalysing oxidation-reduction reactions. The substrate that is oxidised is regarded as hydrogen donor. The systematic name is based on donor: acceptor oxidoreductase. The recommended
20 name will be dehydrogenase, wherever is possible; as an alternative, reductase can be used. Oxidase is only used in cases where O_2 is the acceptor.

Examples of preferred oxidoreductases are oxidases such as glucose oxidase, methanol oxidase, bilirubin oxidase,
25 catechol oxidase, laccase, peroxidases such as ligninase and those described in WO-A-97/31090, monooxygenase, dioxygenase such as lipoyxygenase and other oxygenases as described in WO-A-99/02632, WO-A-99/02638, WO-A-99/02639 and the cytochrome based enzymatic bleaching systems
30 described in WO-A-99/02641.

Peroxidases are used in combination with hydrogen peroxide, which can be formulated into a detergent composition as percarbonate or perborate. The hydrogen peroxide may also be generated during the cleaning and/or rinsing process by an enzymatic system as e.g. described in EP-A-537381.

The activity of oxidoreductases, in particular the phenol oxidising enzymes in a process for bleaching stains on fabrics and/or dyes in solution and/or antimicrobial treatment can be enhanced by adding certain organic compounds, called enhancers. Examples of enhancers are 2,2'-azo-bis-(3-ethylbenzo-thiazoline-6-sulphonate (ABTS) and Phenothiazine-10-propionate (PTP). More enhancers are described in WO-A-94/12619, WO-A-94/12620, WO-A-94/12621, WO-A-97/11217, WO-A-99/23887. Accromonium Murorum Oxidase is example of a phenol oxidase from the subclass of laccases.

Phenol oxidases and peroxidases are preferably used together with a enhancer. The level of enhancer is preferably from 0 to 5000 microM, more preferably from 1 to 2000 microM, more preferably, from 5 to 1000 microM most preferably 10 to 800 microM (per L carbon dioxide).

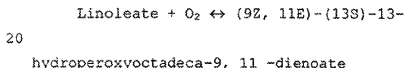
If hydrogen peroxide is used, e.g. with peroxidases, it is preferably used from 0 to 400 mM, more preferably from 0.01 to 200 mM, more preferably from 0.05 to 150 mM, most preferably from 0.1 to 100 mM (per L carbon dioxide).

Preferably, the oxidoreductase according to the invention is selected from oxygen oxidoreductases, hydrogen-peroxide oxidoreductases and mixtures thereof.

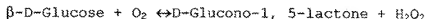
Preferred examples of oxygen oxidoreductases are
 lipoxigenase [EC classification 1.13.11.12], glucose
 oxidase [EC classification 1.1.3.4], maltose oxidase [EC
 5 classification 1.1.3.5] and Accromonium Murorum Oxidase
 (AMO) [EC classification 1.10.3.2]. Examples of hydrogen-
 peroxide oxidoreductases are Arthromyces Ramosus
 Peroxidase; a hemoprotein (ARP) [EC classification
 1.11.1.7] and Chloride peroxidase (CPO) [EC classification
 10 1.11.1.10].

The oxidoreductases can be described by the reaction they
 catalyse.

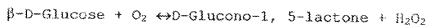
- 15 For example lipoxigenase (Lipoxidase or carotene oxidase,
 systematic name: Linoleate: oxygen 13-oxidoreductase)
 catalyses the following reaction



Glucose oxidase (Glucose oxyhydrase, systematic name:
 β -D-Glucose: oxygen 1-oxidoreductase) catalyses the
 25 reaction
 :

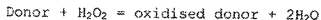


Maltose oxidase (hexose oxidase, systematic name:
 30 D-Hexose: oxygen 1-oxidoreductase) catalyses the reaction



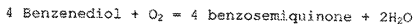
The hemoprotein ARP (systematic name: Donor: hydrogen-peroxide oxidoreductase) catalyses the reaction

5



The laccase AMO (systematic name: Benzenediol: oxygen oxidoreductase) catalyses the reaction

10



The peroxidase CPO (systematic name: Chloride: Hydrogen-peroxide oxidoreductase) catalyses the reaction

15



The inventive composition comprises a bleach-effective amount of oxidoreductase. The exact amount will depend on
 20 the volume of carbon dioxide, number of articles and nature and quantity of stains. The skilled person will be able to determine the bleach-effective amount without undue burden. Preferably, the oxidoreductase is present in the bleaching composition from 1.0×10^{-4} mg/L to 1.0×10^3 mg/L, more
 25 preferably, from 1.0×10^{-3} mg/L to 5.0×10^2 mg/L and even more preferably from 1.0×10^{-2} mg/L to 2.0×10^2 mg/L carbon dioxide.

Surfactants

30 Preferably, the bleach composition according the invention comprises a surfactant. Any surfactant known to the person skilled in the art may be used. Surfactants are described

in US-A-5,789,505, US-A-5,683,977, US-A-5,683,473, US-A-5,858,022 and WO 96/27704. Especially preferred are the surfactants described in WO 96/27704 (formula's I-IV).

5 With regard to the surfactants the following definitions will be used for the present invention. The term "densified carbon dioxide-philic" in reference to surfactants R_nZ_m wherein n and m are each independently 1 to 50, means that the functional group, R_n - is soluble in carbon dioxide at
 10 pressures of from 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C to greater than 10 weight percent. Preferably n and m are each independently 1-35. Such functional groups (R_n -) include halocarbons, polysiloxanes and branched polyalkylene oxides.

15 The term "densified carbon dioxide-phobic" in reference to surfactants, R_nZ_m , means that Z_m - will have a solubility in carbon dioxide of less than 10 weight percent at pressures of from 101 kPa to 68.9 MPa and temperatures of from -78.5
 20 to 100°C. The functional groups in Z_m - include carboxylic acids, phosphatyl esters, hydroxyls, C_{1-30} alkyls or alkenyls, polyalkylene oxides, branched polyalkylene oxides, carboxylates, C_{1-30} alkyl sulphonates, phosphates, glycerates, carbohydrates, nitrates, substituted or
 25 unsubstituted aryls and sulphates.

The hydrocarbon and halocarbon containing surfactants (i.e., R_nZ_m , containing the CO_2 -philic functional group, R_n -, and the CO_2 -phobic group, Z_m -) may have an HLB of less
 30 than 15, preferably less than 13 and most preferably less than 12.

- The polymeric siloxane containing surfactants, R_nZ_m , also designated $MD_xD^*_yM$, with M representing trimethylsiloxyl end groups, D_x as a dimethylsiloxyl backbone (CO_2 -philic functional group) and D^*_y as one or more substituted methylsiloxyl groups substituted with CO_2 -phobic R or R' groups preferably have a $D_xD^*_y$ ratio of greater than 0.5:1, preferably greater than 0.7:1 and most preferably greater than 1:1.
- 10 A "substituted methylsiloxyl group" is a methylsiloxyl group substituted with a CO_2 -phobic group R or R'. R or R' are each represented in the following formula:
- $$-(CH_2)_a(C_6H_5)_b(A)_d-[(L)_e(A')_f]_n-(L')_gZ(G)_h$$
- 15 wherein a is 1-30, b is 0-1, C_6H_5 is substituted or unsubstituted with a C_{1-10} alkyl or alkenyl and A, d, L, e, A', f, n, L', g, Z, G and h are defined below, and mixtures of R and R'.
- 20 A "substituted aryl" is an aryl substituted with a C_{1-30} alkyl, alkenyl or hydroxyl, preferably a C_{1-20} alkyl or alkenyl.
- 25 A "substituted carbohydrate" is a carbohydrate substituted with a C_{1-10} alkyl or alkenyl, preferably a C_{1-5} alkyl. The terms "polyalkylene oxide", "alkyl" and "alkenyl" each contain a carbon chain which may be either straight or branched unless otherwise stated.
- 30 A preferred surfactant which is effective for use in a carbon dioxide bleach composition requires the combination

of densified carbon dioxide-philic functional groups with densified carbon dioxide-phobic functional groups (see definitions above). The resulting compound may form reversed micelles with the CO₂-philic functional groups extending into a continuous phase and the CO₂-phobic functional groups directed toward the centre of the micelle.

The surfactant is preferably present in an amount of less than 10 wt% or more preferably of from 0.001 to 10 wt%, preferably 0.01 to 5 wt%. An especially preferred range is from about 0.03% to about 1 wt%.

If present, the CO₂-philic moieties of the surfactants are preferably groups exhibiting low Hildebrand solubility parameters, as described in Grant, D. J. W. et al. "Solubility Behavior of Organic Compounds", Techniques of Chemistry Series, J. Wiley & Sons, NY (1990) pp. 46-55 which describes the Hildebrand solubility equation, herein incorporated by reference. These CO₂-philic moieties also exhibit low polarisability and some electron donating capability allowing them to be solubilised easily in densified fluid carbon dioxide.

As defined above the CO₂-philic functional groups are soluble in densified carbon dioxide to greater than 10 weight percent, preferably greater than 15 weight percent, at pressures of from 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C.

Preferred densified CO₂-philic functional groups include halocarbons (such as fluoro-, chloro- and fluoro-

chlorocarbons), polysiloxanes and branched polyalkylene oxides.

The CO₂-phobic portion of the surfactant molecule is
 5 obtained either by a hydrophilic or a hydrophobic functional group which is less than 10 weight percent soluble in densified CO₂, preferably less than 5 wt. %, at a pressures of from 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C. Examples of moieties contained in the
 10 CO₂-phobic groups include polyalkylene oxides, carboxylates, branched acrylate esters, C₁₋₃₀ hydrocarbons, aryls which are unsubstituted or substituted, sulphonates, glycerates, phosphates, sulphates and carbohydrates. Especially preferred CO₂-phobic groups include C₂₋₂₀
 15 straight chain or branched alkyls, polyalkylene oxides, glycerates, carboxylates, phosphates, sulphates and carbohydrates.

Preferred surfactants comprise CO₂-philic and CO₂-phobic
 20 groups. The CO₂-philic and CO₂-phobic groups are preferably directly connected or linked together via a linkage group. Such groups preferably include ester, keto, ether, amide, amine, thio, alkyl, alkenyl, fluoroalkyl, fluoroalkenyl and mixtures thereof.

25

A preferred surfactant is:



wherein R_n- is a densified CO₂-philic functional group, R is a halocarbon, a polysiloxane, or a
 30 branched polyalkylene oxide and n is 1-50, and Z_m- is a densified CO₂-phobic functional group, and

m is 1-50 and at pressures of 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C, the R_n - group is soluble in the densified carbon dioxide to greater than 10 wt. percent and the Z_m - group is soluble in the densified carbon dioxide to less than 10 wt. percent. It should be understood that R_n - and Z_m - may be present in any sequence, e.g. RZR, ZRZ, RRRZ, RRRZRZ etc. etc.

Preferably, when R of the surfactant is the halocarbon or the branched polyalkylene oxide, then the surfactant has an HLB value of less than 15. In other cases it may be preferred that when R is the polysiloxane, then the surfactant has a ratio of dimethyl siloxyl to substituted methyl siloxy groups of greater than 0.5:1.

15

Surfactants which are useful in the invention may be selected from four groups of compounds (formula I-IV). The first group of compounds has the following formula:



20

wherein X is F, Cl, Br, I and mixtures thereof, preferably F and Cl;

a is 1 - 30, preferably 1-25, most preferably 5-20;

b is 0 - 5, preferably 0 - 3;

25

c is 1 - 5, preferably 1 - 3;

A and A' are each independently a linking moiety representing an ester, a keto, an ether, a thio, an amido, an amino, a C_{1-4} fluoroalkyl, a C_{1-4} fluoroalkenyl, a branched or straight chain polyalkylene oxide, a phosphato, a sulphonyl, a sulphate, an ammonium and mixtures thereof; d is 0 or 1;

L and L' are each independently a C₁₋₃₀ straight chained or branched alkyl or alkenyl or an aryl which is unsubstituted or substituted and mixtures thereof;

e is 0-3;

5 f is 0 or 1;

n is 0-10, preferably 0-5, most preferably 0-3;

g is 0-3;

o is 0-5, preferably 0-3;

Z is a hydrogen, a carboxylic acid, a hydroxy, a
10 phosphato, a phosphato ester, a sulphonyl, a sulphonate, a sulphate, a branched or straight-chained polyalkylene oxide, a nitril, a glyceryl, an aryl unsubstituted or substituted with a C₁₋₃₀ alkyl or alkenyl, (preferably C₁₋₂₅ alkyl), a carbohydrate unsubstituted or substituted with a
15 C₁₋₁₀ alkyl or alkenyl (preferably a C₁₋₅ alkyl) or an ammonium;

G is an anion or cation such as H⁺, Na⁺, Li⁺, K⁺, NH₄⁺, Ca⁺², Mg⁺²; Cl⁻, Br⁻, I⁻, mesylate, or tosylate; and h is 0-3, preferably 0-2.

20

Preferred compounds within the scope of the formula I include those having linking moieties A and A' which are each independently an ester, an ether, a thio, a polyalkylene oxide, an amido, an ammonium and mixtures
25 thereof;

L and L' are each independently a C₁₋₂₅ straight chain or branched alkyl or unsubstituted aryl; and Z is a hydrogen, carboxylic acid, hydroxyl, a phosphato, a sulphonyl, a sulphate, an ammonium, a polyalkylene oxide,
30 or a carbohydrate, preferably unsubstituted. G groups which are preferred include H⁺, Li⁺, Na⁺, NH₄⁺, Cl⁻, Br⁻ and tosylate.

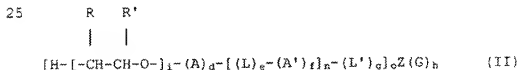
Most preferred compounds within the scope of formula I include those compounds wherein A and A' are each independently an ester, ether, an amido, a polyoxyalkylene oxide and mixtures thereof; L and L' are each independently a C₁₋₂₀ straight chain or branched alkyl or an unsubstituted aryl; Z is a hydrogen, a phosphato, a sulphonyl, a carboxylic acid, a sulphate, a poly(alkylene oxide) and mixtures thereof; and

10 G is H⁺, Na⁺ or NH₄⁺.

Compounds of formula I are prepared by any conventional preparation method known in the art such as the one described in March, J., "Advanced Organic Chemistry", J. 15 Wiley & Sons, NY (1985).

Commercially available fluorinated compounds include compounds supplied as the Zonyl™ series by Dupont.

20 The second group of surfactants useful in the bleach composition are those compounds having a polyalkylene moiety and having a formula (II).



wherein R and R' each represent a hydrogen, a C₁₋₅ straight chained or branched alkyl or alkylene oxide and mixtures thereof;

30 i is 1 to 50, preferably 1 to 30, and

A, A', d, L, L', e, f, n, g, o, Z, G and h are as defined above.

Preferably R and R' are each independently a hydrogen, a C₁₋₃ alkyl, or alkylene oxide and mixtures thereof.

5

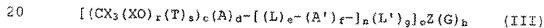
Most preferably R and R' are each independently a hydrogen, C₁₋₃ alkyl and mixtures thereof. Non-limiting examples of compounds within the scope of formula II are described in WO 96/27704

10 Compounds of formula II may be prepared as is known in the art and as described in March et al., *Supra*.

Examples of commercially available compounds of formula II may be obtained as the Pluronic series from BASF, Inc.

15

A third group of surfactants useful in the invention contain a fluorinated oxide moiety and the compounds have a formula:



wherein XO is a halogenated alkylene oxide having C₁₋₆ straight or branched halocarbons, preferably C₁₋₃,

r is 1-50, preferably 1-25, most preferably 5-20,

25 T is a straight chained or branched haloalkyl or haloaryl,

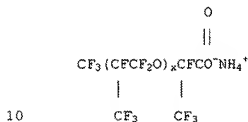
s is 0 to 5, preferably 0-3,

X, A, A', c, d, L, L', e, f, n, g, o, Z, G and h are as defined above.

30

Examples of commercially available compounds within the scope of formula III include those compounds supplied under the Krytox™ series by DuPont having a formula:

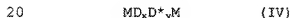
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wherein x is 1-50.

Other compounds within the scope of formula III are made as
15 known in the art and described in March et al., Supra.

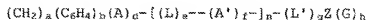
The fourth group of surfactants useful in the invention include siloxanes containing surfactants of formula IV



wherein M is a trimethylsiloxyl end group, D_x is a dimethylsiloxyl backbone which is CO_2 -philic and D^*_y is one or more methylsiloxyl groups which are substituted with a
25 CO_2 -phobic R or R' group,

wherein R and R' each independently have the following formula:

30



wherein a is 1-30, preferably 1-25, most preferably 1-20,

b is 0 or 1,

C_6H_5 is unsubstituted or substituted with a C_{1-10} alkyl or alkenyl, and

A, A', d, L, e, f, n, L', g, Z, G and h are as defined
5 above and mixtures of R and R' thereof.

The $D_x:D_y$ ratio of the siloxane containing surfactants should be greater than 0.5:1, preferably greater than 0.7:1 and most preferably greater than 1:1.

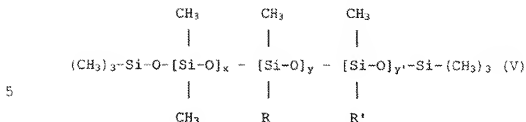
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The siloxane compounds should have a molecular weight ranging from 100 to 100,000, preferably 200 to 50,000, most preferably 500 to 35,000.

15 Silicones may be prepared by any conventional method such as the method described in Hardman, B. "Silicones" the Encyclopaedia of Polymer Science and Engineering, v. 15, 2nd Ed., J. Wiley and Sons, NY, NY (1989).

20 Examples of commercially available siloxane containing compounds which may be used in the invention are those supplied under the ABIL series by Goldschmidt.

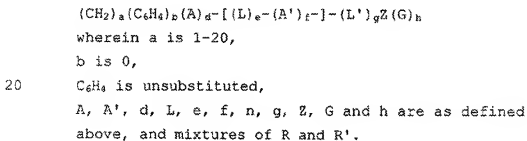
Suitable siloxane compounds within the scope of formula IV
25 are compounds of formula V:



the ratio of x:y and y' is greater than 0.5:1,
 10 preferably greater than 0.7:1 and most preferably greater
 than 1:1, and

R and R' are as defined above.

Preferred CO₂-phobic groups represented by R and R' include
 15 those moieties of the following formula:



Particularly useful surfactants are selected from the group
 25 consisting of the classes of ethoxy modified
 polydimethylsiloxanes (e.g. Silwet™ surfactants from
 Witco), acetylenic glycol surfactants (from Air Products)
 and ethoxy/propoxy block copolymers (e.g. Pluronic™
 surfactants from BASF) and mixtures thereof.

Modifier

In addition to the enzyme-compatible solvent, if present, it may be desirable to include a modifier in the bleaching composition, such as water, or an organic solvent up to only about 20 wt%, and additives to boost the bleaching and or cleaning performance such as enzymes surfactants, perfumes, and antistats, each up to about 10 wt%,.

- 10 In a preferred embodiment, a modifier such as water, or a useful organic solvent may be added with the stained cloth in the cleaning drum in a small volume. Preferred amounts of modifier should be from 0.0 to about 20 wt% (weight/weight of the densified CO₂), more preferably 0.001 to about 10 wt%, even more preferably 0.001 to about 5 wt%, even more preferably 0.01 to about 3 wt%, most preferably from about 0.05 to about 0.2 wt%. Preferred solvents include water, ethanol, acetone, hexane, methanol, glycols, acetonitrile, C₁₋₁₀ alcohols and C₅₋₁₅ hydrocarbons.
- 20 Especially preferred solvents include water, ethanol and methanol. If the modifier is water, optionally 0.1 to 50% of an additional organic cosolvent may be present as described in US-A-5 858 022. In those circumstances it may be preferred to use surfactants as described in US-5 858 022 which do contain a CO₂ philic group.

Method of preparing the bleaching composition

- The oxidoreductase may be added to the bleaching composition in any suitable manner. It may added to the cleaning vessel before or after the carbon dioxide has been let in. The enzyme may also be added in any suitable form to get effective bleaching of the articles. The enzyme may

be added in the form of granules, a dispersion or a solution. Often the dispersion or solution will be formulated to increase the stability of the enzyme.

5 Method of Bleaching

The inventive bleaching method may be used in cleaning systems with carbon dioxide such as described in US-A-5 683 473, US-A-5 676 705, US-A-5 683 977, US-5 881 577, US-A-5 158 704, US-A-5 266 205, US-A-5 858 022 and the references
10 cited therein. According the present invention an effective dry cleaning amount of densified carbon dioxide is used. The exact amount will depend on the volume of the vessel, pressure at which the dry cleaning is performed, number of articles and nature and quantity of stains. The skilled
15 person will be able to determine effective dry cleaning amount of densified carbon dioxide without undue burden using the references above. Usually, the amount of carbon dioxide will correspond to a volume of from 0.1 and 500 litre, more preferably of from 0.2 to 100 litre at the
20 operating pressure and temperature.

The bleaching method may be used to bleach and/or clean any suitable article. The items to be cleaned should be compatible with the densified carbon dioxide. Preferably,
25 the items include garments and domestic articles with hard surfaces. The bleaching method is especially useful to clean textile articles with bleachable stains, in particular those with grass stains.

30 A second aspect of the invention provides a method to bleach articles characterised in that said method comprises

the step of contacting an article with a bleaching composition according to the invention.

Usually, the method of bleaching comprises loading a variety of soiled articles, preferably clothing, into a vessel (preferably a pressurisable vessel) and contacting the articles with the bleaching composition comprising the oxidoreductase. The bleaching composition minus the carbon dioxide may be contacted with the soiled articles before or together with the carbon dioxide. The carbon dioxide may be introduced into the cleaning vessel as described in US-A-5,683,473. Preferably, the carbon dioxide is introduced into the cleaning vessel which is then pressurised to a pressure in the range of about 0.1 to about 68.9 MPa and adjusted to a temperature range of from about -78.5°C up to about 100°C. Although it may not always be desirable, the bleaching method may be carried out in supercritical carbon dioxide where the temperature is between 31°C and 100°C, preferably between 31°C and 60°C. Often it is preferred that the carbon dioxide is in a liquid phase so the temperature is held at - 78.5°C up to about 30°C. Preferably the pressure range is from 0.5 to 48 MPa, more preferably from 2.1 to 41 MPa. Preferably, the temperature range is from -56.2 to 25°C, more preferably from -25°C to 20°C. After the bleaching step, the articles may be rinsed by introducing fresh carbon dioxide into the vessel after removing the bleaching composition.

As described above, one of the advantages of the present invention is that very short bleaching times are needed to obtain good bleaching. Preferably, the articles are

contacted with the bleaching composition for less than 45 min, more preferably less than 35 min, most preferably less 25 min.

The inventive bleaching method may be used in densified 5 carbon dioxide although in some case liquid carbon dioxide may be preferred.

Other than in the examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about". Similarly, all percentages are weight/weight percentages of the carbon dioxide unless otherwise indicated. If the quantity is expressed per volume of carbon dioxide (L), this is the volume carbon dioxide used during the cleaning process. Where the term "comprising" is used in the specification or claims, it is not intended to exclude any terms, steps or features not specifically recited.

The invention is more fully illustrated by the following 10 non-limiting examples showing some preferred embodiments of the invention.

EXAMPLES

15 **Example 1**

The commercially available, bleach sensitive test cloth BC-1 and an oily tomato elefante stained test cloth were dry cleaned using liquid carbon dioxide, oxidoreductases f 20 according to the invention.

BC-1 is a tea stained test cloth made by CFT. Four 2" X 2" swatches of a given stain cloth were placed on the stirrer of a 600 ml autoclave having a gas compressor and an extraction system. An enzyme solution and, if appropriate other additives, was placed on the bottom of the autoclave. The cloths were allowed to move freely in the autoclave. Good agitation was ensured by visual observation with an endoscope through a small sapphire window in the autoclave. After placing the cloths in the autoclave, dosing of the enzyme solution and sealing it, liquid CO₂ at a tank pressure of 5.86 Mpa was allowed into the system and was cooled to reach a temperature of about 12°C at which point the liquid CO₂ was at a pressure of about 5.52 MPa. The stirrer was then turned on for 15 minutes to mimic a wash cycle (300 rpm alternating 5 sec clockwise, 5 sec anti clockwise). At the completion of the wash cycle, 20 cubic feet (566 litre) of fresh CO₂ were passed through the system to mimic a rinse cycle. The pressure of the autoclave was then released to atmospheric pressure and the cleaned cloths were removed from the autoclave. Two runs were performed with each system tested. To measure the extent of cleaning, the cloths were placed in a Reflectometer supplied by Colorguard. The R scale, which measures the reflection of light at 460 nm, was used to determine stain removal. Cleaning results were reported as the percent stain removal according to the following calculation:

$$\% \text{ stain removal} = \frac{\text{stain removed}}{\text{stain applied}} \times 100\%$$

30

$$\frac{\text{cleaned cloth reading} - \text{stained cloth reading}}{\text{unstained cloth reading} - \text{stained cloth reading}} \times 100\%$$

Significant stain removal was observed when the following composition was tested on a BC-1 cloth:

- 5 0.058 mg/L ARP (Arthromyces Ramosus Peroxidase)
- 0.5 mM H₂O₂
- 0.01 wt% PTP: (Phenothiazine-10-Propionic Acid; Mw:271.15)
- 0.5 wt% H₂O
- 0.4 wt% Ethanol

10

Example 2

Significant stain removal was observed when the following composition was tested on a oily tomato stained cloth:

15

- 0.058 mg/L ARP (Arthromyces Ramosus Peroxidase)
- 0.5 mM H₂O₂
- 0.01 wt% PTP
- 0.1 wt% H₂O
- 20 0.08 wt% Ethanol

Example 3

- Significant stain removal was observed when the following
- 25 composition was tested on a BC-1 cloth and an even better stain removal on the oily tomato stained cloth. The latter example was repeated with 3.2 wt% ethanol with similar results.

- 30 19.8 mg/L AMO (Acremonium Murorum Oxidase expressed in Aspergillus awamori)
- 0.01 wt% PTP

14 wt% H₂O

0.4% LES (Sodium Lauryl Ether Sulphate) ex STEPAN

Example 4

5

Significant stain removal was observed when the following composition was tested on a EC-1 cloth

0.70 mg/L CPO (Chloride Peroxidase)

10 1.0mM H₂O₂

To this composition 10μL 50 mM Sodium Vanadate and 1.0 mL 10 mM NaCl was added.

15 **Example 5**

Significant stain removal was observed when the following composition was tested on the oily tomato stained cloth and even better stain removal was found with 1.4 wt% water.

20

34 mg/L Lipoxigenase (Lipoxidase Sigma L-7395 EC

1.13.11.12, from soya bean corresponding to 13.4×10^6 Units/L)

14 wt % water,

25 0.7 wt% ethanol

Example 6

Excellent stain removal was observed when the following composition was tested on the oily tomato stained cloth.

30

8.17 mg/L Glucose oxidase, (Sigma G-6891, 4.9 mg prot./mL,
1200 units/mL from *Aspergillus niger*, EC 1.1.3.4)
1 g/L Glucose: D-(+)-Glucose Sigma G-7528
0.2 wt% water

5

In either of the compositions above 0.05 wt% of the
following surfactant may be used Silwet™ L-7602 (an
organosilicone surfactant from Witco), Pluronic™ L-62 (an
ethoxy/propoxy block copolymer from BASF) or Surfynol™ 440
10 (an ethoxy-modified tertiary acetylenic glycol surfactant
from Air Products).

Claims

1. A bleaching composition comprising
 - a) a bleach-effective amount of an oxidoreductase ;
 - b) 0 to 10 wt% of a surfactant;
 - c) less than 20 wt% of a modifier; and
 - d) an effective dry cleaning amount of densified carbon dioxide.
2. A composition according to claim 1, characterised in that the oxidoreductase is selected from oxygen oxidoreductases, hydrogen-peroxide oxidoreductases and mixtures thereof.
3. A composition according to claim 2, characterised in that the oxidoreductase is selected from the group of phenol oxidases and peroxidases and mixtures thereof.
4. A composition according to claim 2, characterised in that the oxidoreductase is selected from the group consisting of lipxygenase, glucose oxidase, maltose oxidase, Accromonium Murorum Oxidase, Arthromyces Ramosus Peroxidase and Chloride peroxidase and mixtures thereof.
5. A composition according to any preceding claim, characterised in that composition comprises oxidoreductase in an amount of from $1.0 \cdot 10^{-4}$ mg/L to $1.0 \cdot 10^3$ mg/L, more preferably, from $1.0 \cdot 10^{-3}$ mg/L to $5.0 \cdot 10^2$ mg/L and even more preferably from $1.0 \cdot 10^{-2}$ mg/L to $2.0 \cdot 10^2$ mg/L carbon dioxide.
6. A composition according to claim 3, characterised in that the composition further comprises is from 1 to 2000 microM, more preferably, from 5 to 1000 microM, most preferably 10 to 800 microM of an enhancer.

7. A composition according to claim 3 or 6, characterised in that the oxidoreducase is a peroxidase and the composition further comprises from 0.01 to 200 mM, more preferably from 0.05 to 150 mM, most preferably from 0.1 to 100 mM of hydrogen peroxide.

8. A composition according to any preceding claim, characterised in that the composition comprises from 0.001 to 10 wt% of a surfactant.

9. A composition according to claim 8, characterised in that the surfactant is represented by a formula

R_nZ_m wherein

R_n is a densified CO_2 -philic functional group, R is a halocarbon, a polysiloxane, or a branched polyalkylene oxide and n is 1-50;

Z_m is a densified CO_2 -phobic functional group and m is 1-50; and

at pressures of 101 kPa to 68.9 MPa and temperatures of from -78.5 to $100^\circ C$, the R_n - group is soluble in the densified carbon dioxide to greater than 10 wt. percent and the Z_m - group is soluble in the densified carbon dioxide to less than 10 wt. percent.

10. A composition according to any preceding claim, characterised in that the composition comprises 0.001 to about 10 wt% of a modifier.

11. A method to bleach articles characterised in that said method comprises the step of contacting an article with a bleaching composition according to any preceding claim.

12. A method according to claim 11 characterised in that the article is contacted with the composition for less than 45 min, more preferably for less than 35 min.

13. A method according to claims 11 or 12 wherein the articles are textile articles, preferably with grass stains and/or oily tomato stains.



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 Claims searched: 1-13

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, i.e.

UK Cl (Ed.7): DIP (PCBB, PDS, PH)

Int Cl (Ed.7): C11D, D06L

Other: Online: WPI, EPODOC, JAPIO, CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevance to claims
A	US 5676705 (LEVER BROTHERS), see eg. claims 1 and 10	

- ☐ Document indicating lack of novelty or inventive step
☐ Document indicating lack of inventive step if combined with one or more other documents of same category.
☐ Member of the same patent family

- ☐ Document indicating technological background and context of the invention
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☐ Patent document published on or after, but with priority date, before the filing date of this application.